TR-1808—*Cure Studies and Cured Properties of Diglycidyl Ether of 4-Methylolresorcinol (A Rapid-Gelling Epoxy Resin)*, by Allan B. Goldberg, Sheng Yen Lee, and Keith C. Bruce

Cure Studies and Cured Properties of Diglycidyl Ether of 4-Methylolresorcinol (A Rapid-Gelling Epoxy Resin)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Curing was studied of diglycidyl ether of 4-methylolresorcinol (DGEMR), a rapid-gelling epoxy resin synthesized at the Harry Diamond Laboratories. The epoxy, with a built-in catalytic methylol group, can be cured with all types of conventional epoxy hardeners including aliphatic and aromatic amines, anhydrides, polyamidoamines, and polymercaptans. In general, DGEMR gels up to 30 times faster than the regular bisphenol A-type epoxy resins and 2 to 5 times faster than the fastest-gelling commercial epoxies

known. Cures with flexible hardeners such as polyamidoamines and polyoxyalkyleneamines were rapid even at -7°C. Hardening with m-phenylenediamine was complete at room temperature. Adhesion to aluminum obtained with DGEMR formulations was approximately 50 percent greater than that produced by the conventional bisphenol A-type epoxy. Thus, DGEMR appears to be ideal for adhesive, coating, and low-temperature cure applications, as well as for filled formulations without prolonged gel times. However, the methylol substituent appears to enhance water absorption and results in slightly lower electrical resistivity.

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1. INTRODUCTION

The advantages of a rapid-gelling epoxy resin are many. The use of such a resin would decrease hold times in production, reduce disruptions or downtime in repairs, allow the incorporation of fillers without prolonged gel time, and permit broader use of epoxies in general.

Since most conventional epoxy resins require some exposure to heat for complete cures, a manufacturer must possess a significant volume of oven space for curing. A rapid-gelling epoxy resin capable of complete cure at room temperature would not only speed up production, but lead to space and energy savings when ovens are not needed.

Epoxies have found many applications as coatings, paints, and adhesives or "repair" materials. When used for bonding a broken item or as a coating or paint as in highway markings, there is a necessary period of downtime during which the item or highway may not be used. A rapid-gelling epoxy would permit the more rapid return of these things to use.

The curing of an epoxy is an exothermic process. Because the resin is usually a poor thermal conductor, it tends to retain this heat and build up an exotherm. When heat-sensitive objects are being potted, this exotherm must be kept below the critical temperature, frequently 71°C (160°F). One way of staying below this critical temperature is through the use of a filler as a heat sink. However, when fillers are incorporated, the cure rate is retarded, and longer cure times or higher cure temperatures may be required. A rapid-gelling resin would also be expected to cure more slowly when it contains a filler, but would still cure appreciably faster or at lower temperatures than conventional epoxies.

Finally, although epoxies are receiving widespread use in applications at room temperature and above, there are few formulations curable at low temperatures. Thus, with an epoxy resin that gels rapidly at room temperature, a sufficient cure might be obtained at lower temperatures which would extend the benefits of epoxies to cold climates. It would no longer be necessary to use the epoxy in a heated area or to wait for warmer weather.

These, then, were the general reasons that prompted development of a rapid-gelling epoxy resin and led Schmid of the Harry Diamond Laboratories (HDL) to the synthesis of diglycidyl ether of

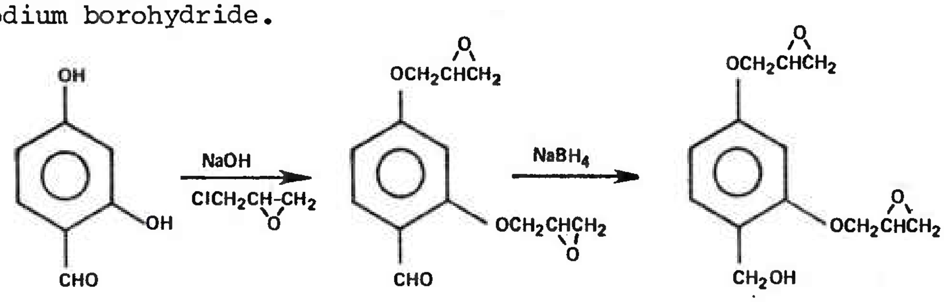
4-methylolresorcinol (DGEMR).[1] The synthesis proceeds from resorcinol in three high-yield steps. A modified Gatterman reaction is used to formylate resorcinol. The β-resorcylaldehyde which results is then condensed with epichlorohydrin in the presence of a base to give diglycidyl ether of β-resorcylaldehyde (DGEBR). This is then reduced either by catalysis or by sodium borohydride to afford DGEMR. The rapid-gelling characters of both DGEMR and DGEBR were demonstrated with diethylenetriamine (DETA).

The purpose of this work was to investigate the rate of cure of DGEMR with conventional epoxy curing agents, such as aliphatic and aromatic amines, polyoxyalkyleneamines, anhydrides, polyamidoamines, and polymercaptans. At the same time, an indication of DGEMR's compatibility with flexibilizers, fillers, and diluents was desired. Finally, physical properties of a number of promising formulations were sought. This information will be the basis for the future development of specific formulations for coatings, adhesives, and potting applications.

2. EXPERIMENTAL

2.1 Resin Preparation and Materials Used

Published procedures were used to prepare DGEMR.[1] A mixture of practical grade β-resorcylaldehyde (I) (Pfaltz and Bauer, Inc., or Eastman Organic Chemicals) and epichlorohydrin was held at reflux during the addition of sodium hydroxide. The product, diglycidyl ether of β-resorcylaldehyde (II) was then reduced to DGEMR (III) by treatment with sodium borohydride.



I II III

Then DGEMR was stored in a freezer to prevent polymerization or viscosity increase before use.

Commercial epoxy resins obtained for comparison include Epon 828, ERE 1359, and Apogen 101. These resins and all other materials used in this study are identified in table I.

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[1] *J. J. Schmid and W. McCarvill, Rapid-Curing Epoxy Resins Derived from Resorcinol, Harry Diamond Laboratories TR-1679 (September 1974); J. J. Schmid, U.S. Patents 3,773,799 (20 November 1973) and 3,925,315 (9 December 1975).*

TABLE I. MATERIALS IN THIS STUDY

Commercial designation	Chemical identity	Source of supply
DGEMR	Diglycidyl ether of 4-methylolresorcinol	HDL synthesis
Epon 828	Diglycidyl ether of bisphenol A	Shell Chemical
ERE 1359	Diglycidyl ether of resorcinol	Ciba-Geigy
Apogen 101	Diglycidyl ether of 2-methylolbisphenol A	M&T Chemicals
DETA	Diethylene triamine	(Various)
DEAPA	Diethylaminopropylamine	(Various)
Jeffamine D230	Polyoxypropylenediamine	Jefferson Chemical
Jeffamine D400	Polyoxypropylenediamine	Jefferson Chemical
Accelerator 298	(Unknown)	Jefferson Chemical
Accelerator 398	(Unknown)	Jefferson Chemical
LP-3	Polysulfide rubber	Thiokol
DER-736	Diglycidyl ether of propylene glycol	Dow Chemical
MPDA	m-Phenylenediamine	GAF
Versamid 140	Polyamidoamine	General Mills
Genamid 2000	Fatty acid amine	General Mills
NMA	Nadic methyl anhydride	Fisher
BDMA	Benzyldimethylamine	Maumee Chemical
TMMA	Tetramethylene maleic anhydride	Anhydrides & Chemicals
Dion DPM 3-800LC	Polyhydroxymercaptan	Diamond Shamrock
DMP-30	2,4,6-Tri(dimethylaminomethyl)phenol	Polysciences

2.2 Characterization of Resins

2.2.1 Weight per Epoxy

Weights per epoxy of these resins were determined by the potassium iodide method.[2] A resin sample of 1.0 to 1.5 g was weighed accurately to 0.001 g into a tared 125-ml Erlenmeyer flask. To the resin was added 25 ml of n-propanol. The mixture was then held at reflux while both 20 drops of an indicating solution (0.1 g bromophenol blue in 99.9 g n-propanol) and 3.0 g of potassium iodide in 5 ml of distilled water were added rapidly. The resulting blue solution was titrated with 1 N hydrochloric acid until a yellow color persisting for 1 min was obtained. The weight per epoxy (WPE) was then calculated by

$$\text{WPE} = \frac{(1000)\ (\text{sample wt, g})}{(\text{ml HCl used})\ (\text{N HCl})}$$

[2] *H. Lee and K. Neville, Handbook of Epoxy Resins, McGraw-Hill Book Co., New York (1967), 4-18.*

2.2.2 Viscosity

Viscosity determinations were done at room temperature by using a series of Gardner bubble viscosity tubes. A sample of the resin was introduced into a standard sample tube until the size of the trapped air bubble approximated the sizes of the bubbles in the reference tubes. The sample and reference tubes were then inverted, and the bubble rise times were compared. If the sample viscosity lay between the viscosities of two reference liquids, the bubble rise times for all three were recorded, and the viscosity of the sample was then determined by interpolation.

2.3 Curing Studies

2.3.1 Determination of Gelation and Hardening

Studies were designed to find the relative gel and hardening times of given formulations; hence, only small masses were used. The gel time was defined as the elapsed time from initial mixing until a wooden probe perpendicularly touching the surface of the resin mass could be removed without material adhering to the probe,[3] as per ASTM D-2471. Hardening time was taken as the elapsed time from initial mixing until a perpendicular hand-held wooden probe would no longer indent the resin surface. Generally, 1 g of resin was mixed with a wooden probe for 1 to 2 min with a stoichiometric amount of the curing agent in a small glass vial 1.4 cm (0.56 in.) in diameter × 4.5 cm (1.75 in.) in height. The vial was set on a glass plate during cure. At periodic intervals, a clean wooden probe was used to test for gelation and hardening.

For curing studies at temperatures below room temperature, the resin portions were weighed into a vial that was then set in dry ice to cool. When the resin was cold, the stoichiometric amount of cooled curing agent was weighed into the vial in a "dry" room (<5 percent relative humidity). Mixing was accomplished with a wooden probe, and the vial was immediately returned to the dry ice for transport to a freezer at -7°C (20°F). Periodically, the curing resin mixture was tested for gelation while still cold. If the mixture was found to be nontacky, it was removed from the freezer, and several milliliters of chloroform were quickly added to the vial. The closed vial was mechanically shaken and then examined for solution of the resin mixture. If the resin mixture did not dissolve, then the freezer storage time was noted as the gel time. In vials where no gelation had occurred, the mixture was rapidly disintegrated or dissolved in the chloroform.

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[3]*1972 Annual Book of ASTM Standards, Part 26, American Society for Testing and Materials, Philadelphia, PA (1972), 538-540.*

2.3.2 Determination of Peak Exotherm during Cure

Studies to determine peak exotherm during cure used masses, each totaling 30 g, to simulate potting or encapsulating situations. Stoichiometric amounts of the resin and curing agent were mixed in a 50-ml beaker. When mixing was complete, a glass-enclosed thermocouple was embedded near the center of the mass, and the temperature was monitored with a recorder to determine peak exotherm and the time at which the peak occurred. In some instances, gelation and hardening times of these masses also were recorded as in section 2.3.1.

2.4 Tensile Strength

Tensile strengths were measured[4] according to ASTM D-638. Type IV specimens were cast in silicone molds, cured, and machined to an approximate thickness of 0.41 cm (0.16 in.).

2.5 Adhesive Strength

Adhesive tensile tests were performed on aluminum rod specimens having diameters of 1.429 cm (0.5625 in.). The rods were vapor degreased with chlorothene and then treated at room temperature for 30 min with a solution of 30 parts water, 10 parts concentrated sulfuric acid, and 1 part sodium dichromate. They were then washed well with distilled water and air dried. The resin mixture to be tested was applied to the end surfaces of a set of six rods clamped in special alignment fixtures. Following removal of air bubbles from the resin in a vacuum chamber, a second set of six rods was placed in contact with the coated surfaces, and a clamping pressure was applied by spring-loaded plungers. Flash at the adhesive joint was removed by wiping with a paper towel. The specimens were cured, and the adhesion tests were run[5] according to ASTM D-2095.

2.6 Shore Hardness

Hardness measurements were made[4] with a Shore D durometer according to ASTM D-2240.

2.7 Water Absorption

The amount of water absorbed by resin samples 5.08 cm (2.00 in.) in diameter and 0.318 cm (0.125 in.) thick was determined[4] according to ASTM D-570.

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[4] *1972 Annual Book of ASTM Standards, Part 27, American Society for Testing and Materials, Philadelphia, PA (1972); 185-198; 658-661; 165-168.*

[5] *1969 Annual Book of ASTM Standards, Part 16, American Society for Testing and Materials, Philadelphia, PA (1969), 727-730.*

2.8 Volume Resistivity

Volume resistivity measurements were taken[4] on samples, 4.999 cm (1.968 in.) in diameter and 0.508 cm (0.200 in.) thick, according to ASTM D-257. Electrode diameters[4] were 2.54 cm (1.00 in.) (D_1) and 3.81 cm (1.50 in.) (D_2). A Guideline Model 9520 Digital Teraohmmeter was used for readings at 500 V.

3. RESULTS AND DISCUSSION

3.1 Properties of Resin

The WPE of DGEMR was determined by a known method to ascertain the resin's purity and its reactivity toward curing agents. The values obtained are nearly 50 percent greater than the theoretical value of 126. The greater values can be attributed to the existence of some oligomers formed in the preparation process. Also, they could be caused at least in part by the possible side reaction of oxirane-ring opening in the $NaBH_4$ reduction, since the oxirane ring is unusually active due to the neighboring methylol group. Indeed, a doublet at 1.27 ppm was noted in the nmr spectra of some batches of DGEMR. This doublet appears to fit the methyl proton in $-OCH_2CH(OH)CH_3$, formed after ring opening. The higher WPE was generally reflected by a higher viscosity. A lower viscosity or WPE was usually obtained when the temperature of the reaction mixture was kept below 15°C (59°F) while the $NaBH_4$ was added as quickly as possible and the reduction reaction was quenched within 30 min.

The presence of small amounts of residual chloroform from the reduction work-up also interferes with accurate measurement of both the weight per epoxy and the viscosity. For this reason, solvent removal was accomplished with slight warming on a rotary evaporator under a vacuum of about 266 Pa.

The viscosity of one batch was monitored over 120 days at room temperature. The change in viscosity with time is shown in figure 1. Apparently, the activated nature of the oxirane rings in DGEMR causes the resin to possess a relatively high tendency of polymerization with a consequent viscosity increase on standing at room temperature. To increase its shelf life, the resin should therefore be stored at lower temperatures. At -14°C (7°F), no viscosity increase was noticed over 6 months. As shown in table II, the reactive Apogen 101 was so viscous that heating or adding a solvent was necessary to make a viscosity

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[4] *1972 Annual Book of ASTM Standards, Part 27, American Society for Testing and Materials, Philadelphia, PA (1972), 90-110.*

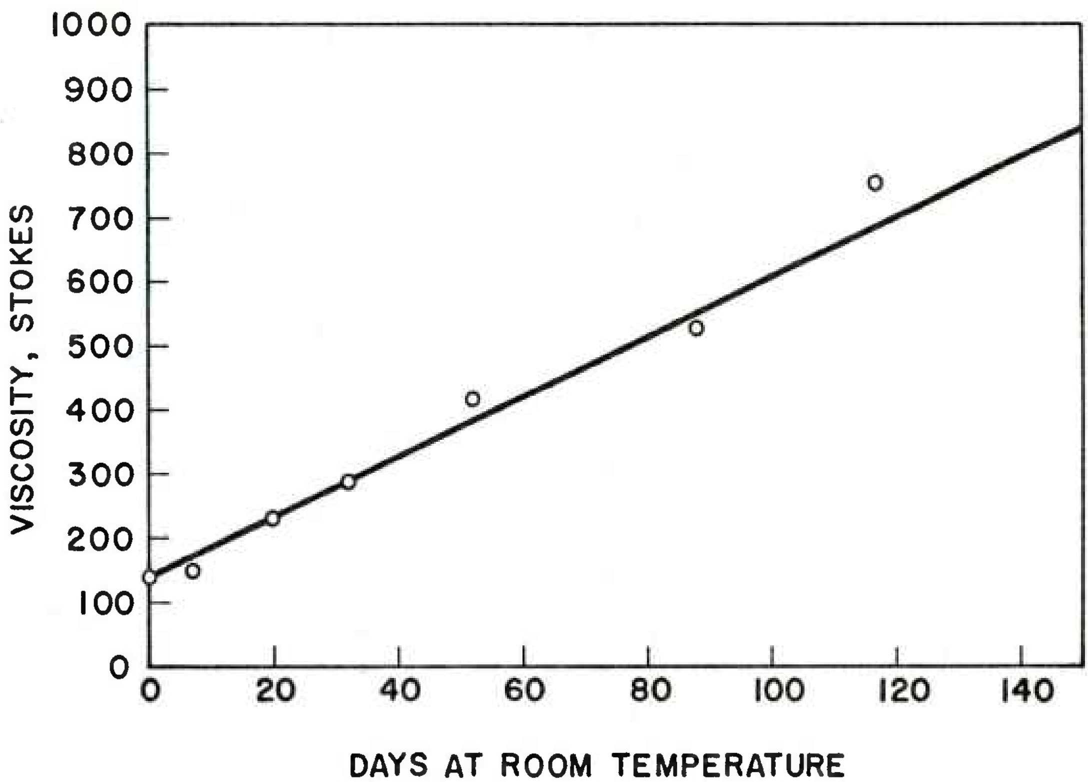

Figure 1. Increase of viscosity of stored DGEMR with time.

TABLE II. VISCOSITIES OF COMPARISON RESINS AT ROOM TEMPERATURE

Resin[a]	Viscosity		Weight per epoxy
	Poises	Stokes	
DGEMR	(No data)	138-220	158-185
Epon 828[b]	100-160	86-137	185-192
Apogen 101[c]	3-7[d]	2.8-6.5[d]	205-225
	80-110[e]	(No data)	
ERE 1359[f]	3-5	2.4-4.1	127

[a] *See table I for material identification.*
[b] *Epon Resins for Casting, Shell Chemical Co. (1967), 7.*
[c] *Apogen 101--A Fast Cure Epoxy Resin, Technical Data Sheet No. 313, M&T Chemicals, Inc. (1972).*
[d] *80% in methyl isobutyl ketone.*
[e] *50°C.*
[f] *Ciba ERE 1359--A Resorcinol Digylcidyl Ether, Technical Bulletin CR 145, Ciba Products Co. [n.d.].*

measurement,[6] whereas the viscosity of DGEMR is close[7] to that of Epon 828. Also, DGEMR does not tend to crystallize as does[8] ERE 1359. Thus, DGEMR is a reactive resin, but it can be handled in about the same way as a conventional epoxy.

3.2 Cure Studies

3.2.1 Comparison of Cure Rates at and below Room Temperature

The ability of DGEMR to cure with a wide variety of conventional epoxy curing agents was studied. Gel and hardening times with aliphatic and aromatic amines are presented in table III. Similar data for cure with polyamidoamines are given in table IV and with anhydrides in table V. For cures at temperatures below room temperature, the results are recorded in table VI. For comparison, the corresponding gel and hardening times of the commercial epoxies Epon 828, ERE 1359, and Apogen 101 also were determined, and the comparison is shown graphically in figure 2. Epon 828 is a standard bisphenol A-type epoxy. The other two epoxies are known in the market as rapid gelling. Like DGEMR, ERE 1359 is based on resorcinol, but without the methylol substituent. Apogen 101 is similar to Epon 828, but is modified with a methylol substituent on one of its two aromatic rings. In all studies, DGEMR was found to gel and cure up to 30 times faster with a given hardener than did Epon 828 and 2 to 5 times faster than did Apogen 101.

The behavior of DGEMR with anhydrides is of particular note. With Nadic methyl anhydride (NMA), Epon 828 required exposure to heat in order to gel. In less than 1 week, DGEMR was completely hardened to a wooden probe at room temperature. With tetramethylene maleic anhydride (TMMA), DGEMR gelled and hardened in approximately 1/3 the time needed for Epon 828. However, with both curing systems, a postcure of DGEMR at elevated temperatures was found necessary to develop better properties.

The curing studies at low temperature suggest that DGEMR's reactivity would be useful in field operations where cold would prevent successful use of conventional epoxies. Even with the small masses used here (1 g), positive cure of DGEMR was obtained at temperatures as low as -7°C (20°F) with two flexible curing systems, a polyoxypropyleneamine and a polyamidoamine. Larger masses should cure readily with attainment of good physical strength.

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[6]*Apogen 101--A Fast Cure Epoxy Resin, Technical Data Sheet No. 313, M&T Chemical, Inc., Rahway, NJ (1972).*

[7]*Epon Resins for Casting, Shell Chemical Co., New York (1967), 7.*

[8]*Ciba ERE 1359--A Resorcinol Diglycidyl Ether, Technical Bulletin CR 145, Ciba Products Co., Summit, NJ [n.d.].*

TABLE III. GEL AND HARDENING TIMES AT ROOM TEMPERATURE OF 1-g MASSES OF RESINS WITH ALIPHATIC AND AROMATIC AMINES, AS DETERMINED BY WOODEN PROBE

Resin[a]	Hardener (phr)	Additives (phr)	Gel time (hr)	Hardening time (hr)
DGEMR	DETA (11)	--[b]	0.08	<3.0
Epon 828	DETA (11)	--	2.75	3.25
Apogen 101	DETA (8)	--	5.0	(No data)
DGEMR	DEAPA (38)	--	0.75	1.0
Epon 828	DEAPA (10)	--	10.5	23
Apogen 101	DEAPA (23)	--	2.5	(No data)
DGEMR	DEAPA (8)	LP-3 rubber (43)	0.93	5.0
Epon 828	DEAPA (10)	LP-3 rubber (43)	10.5	23
DGEMR	Jeffamine D230 (30)	--	1.0	2.5
Epon 828	Jeffamine D230 (30)	--	18.75	22.75
Apogen 101	Jeffamine D230 (24)	--	5.5	7 to 50
ERE 1359	Jeffamine D230 (48)	--	14	18
DGEMR	Jeffamine D230 (26.5)	Accelerator 298 (5.3)	0.70	1.50
DGEMR	Jeffamine D230 (26.5)	Accelerator 298 (5.3), DER 736 (30)	2.65	<18
DGEMR	Jeffamine D400 (48.5)	Accelerator 298 (9.7)	1.37	5.5
Epon 828	Jeffamine D400 (40.5)	Accelerator 298 (8.1)	(No data)	7 to 23
DGEMR	MPDA (35)	--	0.75	1.0
Epon 828	MPDA (32)	--	7.0	(No data)

[a] *See table I for material identification.*
[b] *-- means no additive included.*

TABLE IV. GEL AND HARDENING TIMES AT ROOM TEMPERATURE OF 1-g MASSES OF EPOXY RESINS WITH POLYAMIDOAMINES, AS DETERMINED BY WOODEN PROBE

Resin[a]	Hardener (phr)	Gel time (hr)	Hardening time (hr)
DGEMR	Versamid 140 (40)	1.0	2.33
DGEMR	Genamid 2000 (40)	0.33	0.75
Epon 828	Genamid 2000 (40)	(No data)	5.0
Apogen 101	Genamid 2000 (25)	0.67	2.25

[a] *See table I for material identification.*

TABLE V. GEL AND HARDENING TIMES AT ROOM TEMPERATURE OF 1-g MASSES OF EPOXY RESINS WITH ANHYDRIDES, AS DETERMINED BY WOODEN PROBE

Resin[a]	Hardener (phr)	Gel time (hr)	Hardening time (hr)
DGEMR	NMA (110)/BDMA (1)	41	48 to 138
Epon 828	NMA (90)/BDMA (1)	(*b*)	69 + 4 hr at 70°C + 1 hr at 155°C
DGEMR	TMMA (97)/BDMA (1)	23	32 to 96
Epon 828	TMMA (80)/BDMA (1)	94 to 166	190 to 214

[a]*See table I for material identification.*
[b]*Still fluid after 69 hr.*

TABLE VI. GEL TIMES OF 1-g MASSES OF EPOXY RESINS AT -7°C

Resin[a]	Hardener (phr)	Gel time (hr)
DGEMR	Jeffamine D230 (26.5) + Accelerator 398 (5.3)	39
Epon 828	Jeffamine D230 (26.5) + Accelerator 398 (5.3)	>>360[b]
DGEMR	Genamid 2000 (40)	8
Epon 828	Genamid 2000 (40)	>48[b]

[a]*See table I for material identification.*
[b]*Completely soluble in chloroform when checked after the hours indicated.*

One system, not included in table VI, that produced rapid room temperature gelation of a 1-g mass was a 90:10 mixture of Dion DPM 3-800LC (a polysulfide) and DMP-30 (an aminophenol). With conventional epoxy resins, this curing system gives what is known as a "5-min epoxy."[9] Epon 828 with 66 phr of this mixture gelled in 4 min, Apogen 101 plus 10-percent butyl glycidyl ether with 100 phr gelled in 2.5 min, and DGEMR with 66 phr gelled in 1.5 min. This Dion curing system appears to give the most rapid gelation with this mass of resin without suffering excess exotherms and, hence, would be promising as an adhesive or coating material.

[9]*Physical Properties of Dion Polymercaptan DPM 3-800LC Resin Quick-Cure Epoxy Hardener in Epoxy/Amine and Epoxy/Polyamide Systems, Technical Information Sheet PL-LC-1, Diamond Shamrock Chemical Co., Cleveland, OH [n.d.].*

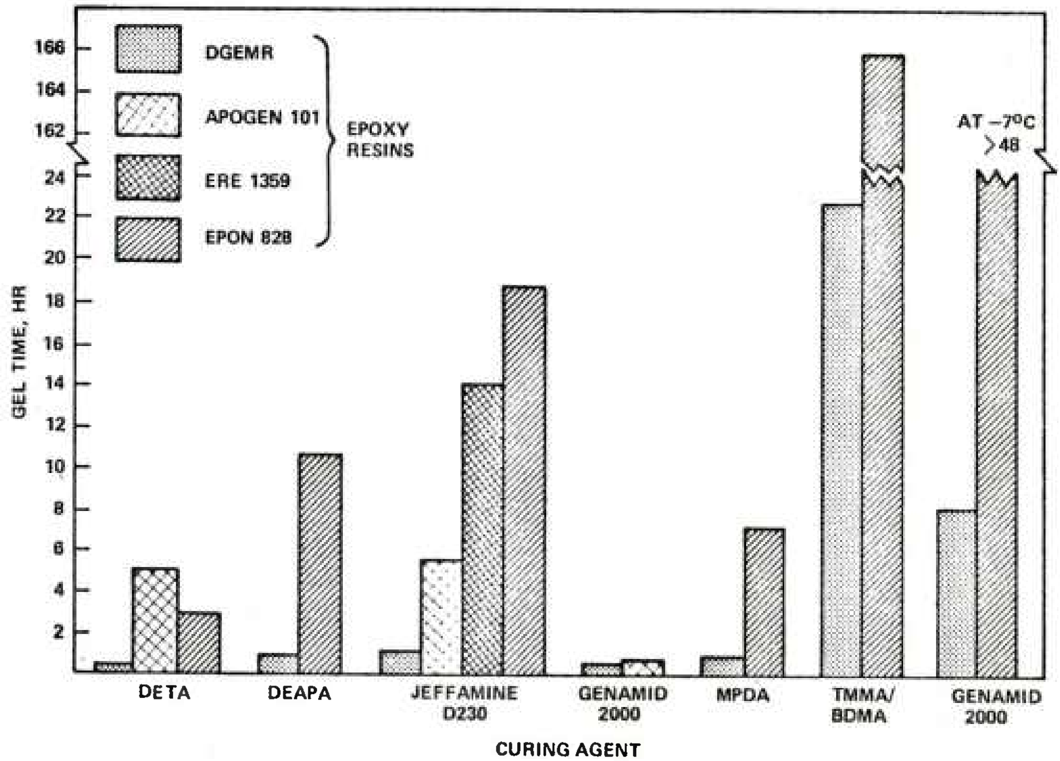

Figure 2. Relative gel times at room temperature for epoxy resins.

Of the various curing agents investigated, the most attractive one was Jeffamine D230, a polyoxypropyleneamine.[10] This hardener produced rapid gelation while still giving an adequate amount of time for thorough mixing and application. Further, the long chains of the polyoxypropyleneamine allow it to act as a flexibilizer, as well as a curing agent. Consequently, this system was selected for a closer look at its cured properties.

3.2.2 Exotherm

As would be expected from their relative reactivities, DGEMR produced significantly higher peak exotherm temperatures than the comparison resins when cured with Jeffamine D230, as shown in table VII. In practical use, the peak exotherm temperature could be lowered by heat sinks or by the inclusion of a filler. Fillers in standard bisphenol A-type epoxies normally serve to lower the exotherm, sometimes to the

[10] *Jeffamine Polyoxypropyleneamines, Advance Technical Data, Jefferson Chemical Co., Inc., Houston, TX (1969).*

TABLE VII. EXOTHERM STUDIES ON 30-g TOTAL MASSES

Resin[a]	Jeffamine D230 (phr)	Peak temp (°C)	Peak time (hr)	Gel time (hr)
Epon 828	30	28.1	(No data)	(No data)
DGEMR	30	145.0	0.21	0.22
ERE 1359	30	40.9	3.0	(No data)
Apogen 101	24	50.0	0.5	4.32

[a]*See table I for material identification.*

extent that a full cure at room temperature is difficult to obtain. While some retardation of cure rate by fillers is expected also with DGEMR, this resin's reactivity should make a room temperature cure much more likely.

3.3 Cured Properties

3.3.1 Mechanical Properties

Tensile tests were run on DGEMR and Epon 828, each cured with 30 phr of Jeffamine D230, one of the most attractive curing agents. A cure cycle of 24 hr at room temperature followed by 4 hr at 70°C (158°F) was used to give a reasonable assurance of full cure for all systems being compared. The average tensile strengths at rupture were 82,000 kPa (11,900 psi) for DGEMR and 55,000 kPa (8,000 psi) for Epon 828. Average elongations were 5.6 and 5.4 percent, respectively. Thus, with this curing agent, the tensile strength of DGEMR is nearly 50 percent greater than that of a bisphenol A-type epoxy, with no effect on the ultimate elongation. This behavior reflects the greater cross-link density produced by the mononuclear DGEMR versus the larger bisphenol A molecule.

The results of adhesive tensile tests are presented in table VIII. With aluminum adherends, DGEMR consistently proved to be a stronger adhesive than Epon 828--from 7 to 476 percent stronger. Again, the greater cross-link density of the DGEMR relative to that of Epon 828 is likely a contributing factor. In addition, the polar methylol groups probably also promote the adhesive strength of the cured resin.

TABLE VIII. ADHESIVE TENSILE STRENGTHS OF EPOXY RESINS ON ALUMINUM ADHERENDS.

Resin[a]	Hardener (phr)	Cure cycle	Adhesive tensile strength	
			(kPa)	(psi)
DGEMR	Jeffamine D230 (40)	92 hr at room temp	81,400	11,800
Epon 828	Jeffamine D230 (30)	+ 4 hr at 70°C	59,600	8,650
DGEMR	Jeffamine D400 (48.5)/ Accelerator 298 (9.7)	41 hr at room temp	91,700	13,300
Epon 828	Jeffamine D400 (40.5)/ Accelerator 298 (8.1)	+ 4 hr at 70°C	85,500	12,400
DGEMR	Versamid 140 (63)	44 hr at room temp	68,300	9,910
Epon 828	Versamid 140 (40)	+ 4 hr at 70°C	11,900	1,720
DGEMR	NMA (110)/BDMA (1)	24 hr at 70°C	24,800	3,590
Epon 828	NMA (90)/BDMA (1)	+ 4 hr at 200°C	18,200	2,635

[a]*See table I for material identification.*

3.3.2 Water Absorption and Other Properties

Due to the presence of a methylol substituent in the DGEMR molecule, DGEMR is inherently more hydrophilic than the conventional bisphenol A-type epoxy, as demonstrated by the water absorption data shown in table IX. As tested, DGEMR cured with Jeffamine D230 absorbs water eight to nine times faster than Epon 828 similarly cured. The faster water absorption resulted in significant degradation of hardness. Both cured systems had about equal Shore D hardness, 84 to 88, at the beginning of the test. The hardness of the cured DGEMR showed a noticeable decrease after 24-hr water immersion and dropped to 62 after 1-week immersion. Over the same 1-week period, the cured Epon 828 showed little change.

The influence of the methylol group was shown also in the electrical properties. Cured with Jeffamine D230, DGEMR had a volume resistivity of 6.1×10^{12} ohm-cm, whereas Epon 828 had 3.3×10^{14} ohm-cm. With the NMA/benzyldimethylamine (BDMA) curing system, the resistivity values were 3.3×10^{13} ohm-cm for DGEMR and 3.4×10^{15} ohm-cm for Epon 828. The greater hydrophilicity of the DGEMR versus that of the Epon 828 would be expected to result in a faster decrease, and one of greater magnitude, in volume resistivity on exposure to water.

TABLE IX. WATER ABSORPTION OF EPOXY RESINS CURED WITH JEFFAMINE D230

Time submerged	Weight gain (%)		Hardness (Shore 0)	
	OGEMR[a]	Epon 828[a]	OGEMR[a]	Epon 828[a]
0 hr	(No data)	(No data)	88	84
2 hr	0.36	0.041	(No data)	(No data)
24 hr	1.27	0.162	80	85
1 week	3.68	0.413	62	85
3 weeks	6.49	0.752	(No data)	(No data)

[a]*See table I for material identification.*

3.4 Comparison of DGEMR with Reference Resins

3.4.1 Comparison of DGEMR with Epon 828

For easier reference, the properties of both DGEMR and Epon 828 cured with Jeffamine D230 have been collected in table X. The uncured epoxies have similar weights per epoxy and viscosities and may be handled very much alike. However, DGEMR is nearly 19 times more reactive than Epon 828. This rapid cure rate releases a substantial amount of heat energy in a short period of time, producing a high exotherm for DGEMR. In tensile strength and adhesive tensile strength, DGEMR appears to be nearly 50 percent stronger than Epon 828, while suffering no decrease in elongation. The methylol groups which serve to activate the oxirane rings also decrease the volume resistivity of DGEMR relative that of to bisphenol A-type epoxy. Further, they increase the rate of water absorption, thereby causing a decrease in Shore D hardness on exposure to water.

TABLE X. COMPARISON OF PROPERTIES OF DGEMR AND EPON 828 CURED WITH JEFFAMINE D230

Property	DGEMR[a]	Epon 828[a]
Viscosity of resin, Stokes	138 to 220	86 to 137
Weight per epoxy	158 to 185	185 to 192
Gel time, hr (1-g mass, room temp)	1.0	18.75
Hardening time, hr (1-g mass, room temp)	2.5	22.75
Gel time, hr (30-g mass, room temp)	0.22	No data
Peak temp during cure, °C (30-g mass)	145	28.1
Hardness, Shore D, initial	88	84
after 24 hr in water, room temp	80	85
Tensile strength, kPa (psi) (ASTM D-638)[b]	82,000 (11,900)	55,000 (8,000)
Elongation at rupture, % (ASTM D-638)[b]	5.6	5.4
Adhesive tensile strength, kPa (psi) (Al rods, ASTM D-2095)[c]	81,400 (11,800)	59,600 (8,650)
Water absorption, % weight gain (ASTM D-570)[d]		
After 2 hr in water, room temp	0.36	0.041
After 24 hr in water, room temp	1.27	0.162
Volume resistivity, ohm-cm (ASTM D-257)[e]	6.1×10^{12}	3.3×10^{14}

[a] *See table I for material identification.*

[b] *1972 Annual Book of ASTM Standards, Part 27, American Society for Testing and Materials, Philadelphia, PA (1972), 185-198.*

[c] *1969 Annual Book of ASTM Standards, Part 16, American Society for Testing and Materials, Philadelphia, PA (1969), 727-730.*

[d] *1972 Annual Book of ASTM Standards, ibid., 165-168.*

[e] *Ibid., 90-110.*

3.4.2. Advantages of DGEMR over Comparison Epoxy Resins

The single greatest advantage of DGEMR over the comparison resins tested here is in accelerated gel and cure rates. For example, DGEMR gels up to 30 times faster than does a conventional bisphenol A-type epoxy such as Epon 828. It is two to five times faster than Apogen 101, the fastest-gelling epoxy known commercially. It can cure at temperatures down to -7°C (20°F) with a number of curing agents, opening field applications in cold climates to the inherent advantages of epoxy resins.

A second major advantage is in DGEMR's ease of handling. It is as easy to handle as Epon 828 and more convenient than either ERE 1359 or Apogen 101. As a liquid at room temperature, it does not have to be warmed before use as with the solid ERE 1359. Its viscosity is much lower than that of Apogen 101, so that dilution with a solvent or reactive diluent is necessary only when thin coats are desired.

Improved tensile strength and adhesion are obtained with DGEMR in place of Epon 828. Use of DGEMR will be especially advantageous in small masses or thin films, such as with coatings and adhesives where negligible exotherm buildup would normally produce slow cures. The low viscosity of DGEMR also makes it useful for formulations requiring fillers or additives, without prolonging the gel time to an intolerable degree.

3.4.3 Advantages of Comparison Epoxy Resin over DGEMR

While DGEMR's inherent reactivity produces rapid gelation, it also can cause increasing viscosity during storage at room temperature and, thus, DGEMR is best kept at lower temperatures. Another disadvantage of DGEMR relative to conventional bisphenol A-type epoxy resins is in DGEMR's greater propensity for water absorption. This could affect its performance in some applications.

4. CONCLUSIONS

A rapid-gelling epoxy resin, DGEMR can be cured with all types of conventional epoxy curing systems such as aliphatic and aromatic amines, polyamidoamines, anhydrides, and polysulfides. The cured DGEMR showed higher tensile and adhesive tensile strengths than the cured Epon 828. It has high potential for applications such as coating, adhesive bonding, filled encapsulations, and uses where low-temperature cure is desired.

Efforts should be aimed at the improvement of the resin preparation procedure and the formulation of the resin for specific applications. Development of a good catalytic reduction to replace the hydride reduction method would lower the production cost. Purification of crude DGEMR through an efficient wipe-film distillation could remove more oligomers and, consequently, lower the WPE and viscosity.

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